Geochemical evolution of the permeable-impermeable boundary within the Earth's crust revealed by silica precipitation

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論 文 内 容 要 旨

1. Introduction

Silica is one of the dominant constituents of the Earth's crust. Silica minerals are generically called "silica polymorphs" that have the same chemical composition, SiO_2, but its crystal structure is different each other. Quartz is the most stable phase of silica in the Earth's crust and also a common mineral in hydrothermal veins. Diagenesis of silica polymorphs has been expected as the change of amorphous silica (opal-A) → cristobalite (opal-C/CT) → quartz.

The transition zone of the rock strength is known as the brittle-plastic transition (BPT). Temperature at the BPT is mainly 300–450 ℃ (Scholz, 2002). The boundaries of the seismic-aseismic and the permeable-impermeable zones correspond to the BPT. Ubiquitous occurrence of quartz vein is one of the evidences that the spatial and temporal variations in permeability within the Earth's crust are affected by silica precipitation in aqueous fluids. However, the role of dissolution and precipitation of silica minerals on fracture permeability and earthquakes is still unclear.

2. The hydrothermal experiments of silica precipitation

The hydrothermal flow-through experiments were conducted to investigate the temperature dependence and the effect of minor components in the solution on silica precipitation in the supercritical conditions of water. No rock/mineral substrate was set in the precipitation vessel.

The experiments of temperature dependence revealed that large amount of silica precipitation occurs only in supercritical conditions at 24 and 31 MPa, whereas less precipitation of silica minerals occurs in liquid phase (Fig. 1). Strong temperature dependence can be explained by the homogeneous nucleation of quartz in the surface energy of quartz, $\sigma = 130$ mJ/m^2.

The experiments of minor components in the solution revealed that the dominant precipitates changes

systematically with increasing Al concentration in the input solution from 0 to 29 mg/kg(H_2O): amorphous silica → cristobalite → quartz → albite and analcite (Fig. 2). In the experiments of Al concentration in the input solution of 6 and 7 mg/kg(H_2O), no relics of precipitation of amorphous silica was found within quartz crystals (Fig. 3). The precipitation rate increases with increasing of Al concentration in the input solution from 0 to 7 mg/kg(H_2O). The accompanying change in the solution chemistry and the composition of the precipitated products indicates that Al coupled with Na is incorporated into the silica minerals.

3. The kinetic equation of overall silica precipitation

The empirical kinetic equation of overall silica-water interaction, including surface reaction of quartz and nucleation of silica minerals, was proposed. The first term of the new kinetic equation is the kinetic equation of surface reaction (Rimstidt and Barns, 1980). The rate constant of surface reaction is given by Okamoto *et al.* (2010). The kinetic equation of overall silica-water reactions is determined as follows:

$$\frac{\partial C_{\mathrm{Si}}}{\partial t} = \left\{ \frac{A_{\mathrm{Qtz}}}{M} k_{\mathrm{S}} + \alpha k_{\mathrm{N}} \right\} \left(C_{\mathrm{Si,Qtz,eq}} - C_{\mathrm{Si}} \right) \qquad (1)$$

where C_{Si} and $C_{\mathrm{Si,Qtz,eq}}$ is the concentration of Si and quartz solubility (mg/kg(H_2O)), respectively, t is time (sec), k_{S} and k_{N} are the rate constant of surface reaction and nucleation (kg m^{-2} sec^{-1}), respectively, A_{Qtz} is the reaction surface area of quartz (m^2), M is the mass of water in the system (kg), and α is the nucleation parameter.

Based on the precipitation experiments of flow rate, the nucleation-controlled precipitation of silica minerals is expressed in a first order rate equation. The nucleation parameter is 1 only in the Si supersaturated solution with respect to quartz and in the supercritical conditions of

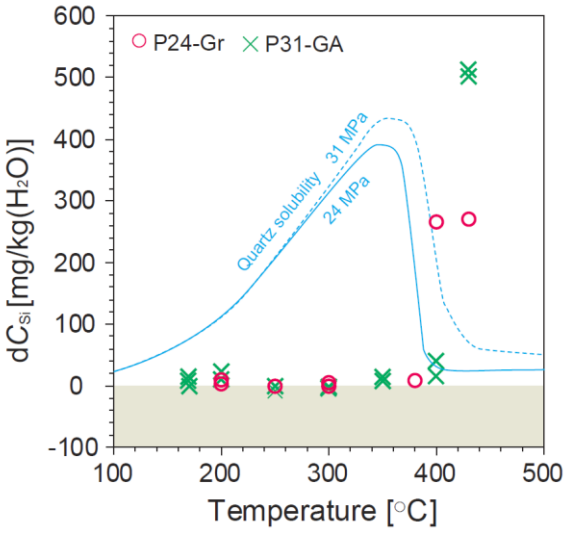

Figure 1 Temperature of precipitation and difference of Si concentrations between the input and output solutions. Red circles show the precipitation experiment at 24 MPa and green crosses show the precipitation experiment at 31 MPa. The grey line and the grey broken line show the solubility of quartz at 24 MPa.

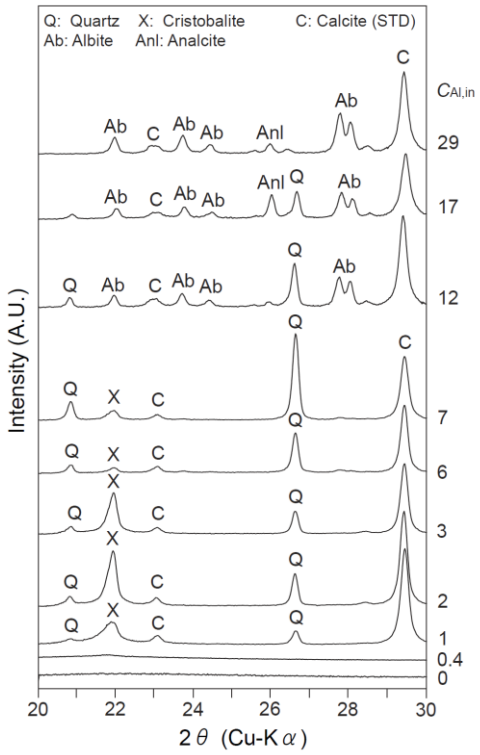

Figure 2 XRD results of precipitated products. Observed minerals were quartz (Q), cristobalite (X), albite (Ab), and analcite (Anl). Calcite (C) at 2θ = 29.4° was used as the standard material for estimate the relative intensity.

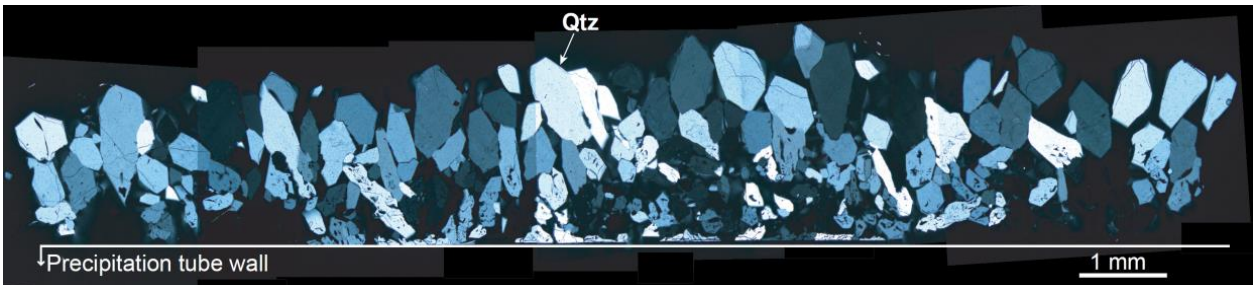

Figure 3 Photomicrograph of the thin sections of precipitated quartz in the experiment of $C_{Al,in}$ = 6 mg/kg(H_2O) under cross-polarized light.

water. The rate constant of nucleation is derived as a function of Al concentration in the solution. The experimental results of silica precipitation without rock/mineral substrates could be simulated well by the new kinetic equation of overall silica reaction.

4. Silica precipitation at the permeable-impermeable boundary

The hydrological system within Earth's crust is divided into the permeable zone and the underlying, much less permeable zone. The Kakkonda geothermal field, Japan, has the well WD-1a that penetrated the boundary between the hydrothermal convection zone and the heat conduction zone. Calculation of quartz solubility along the well WD-1a revealed that the depth of a local minimum of quartz solubility correlates with that of the hydrological boundary at ~3100 m depth (380 °C, 24 MPa) (Fig. 4), in either case of hydrostatic conditions or of fluid pressure increase above hydrostatic at deeper levels. The results of the hydrothermal experiments of silica precipitation and the calculation of silica solubility in this study suggested that rapid quartz precipitation could occur via nucleation when fluids are brought from the liquid region to the supercritical region. The preferential precipitation of quartz at a specific depth plays a significant role in forming and sustaining the permeable-impermeable boundary in the Earth's crust.

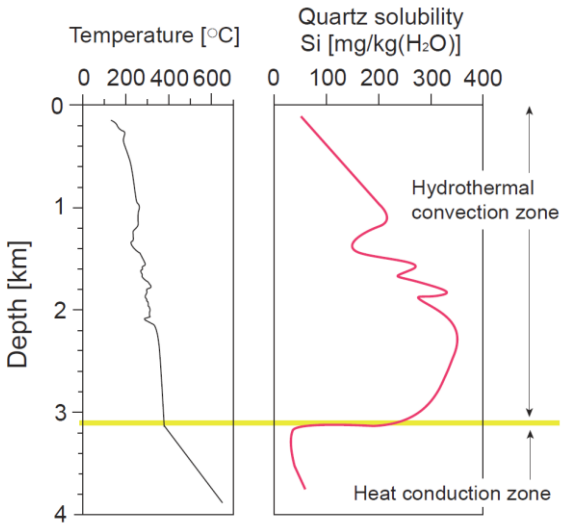

Figure 4 (a) Temperature in the Kakkonda geothermal field (Ikeuchi *et al*., 1998), and (b) quartz solubility calculated by using the program LonerAP (Akinfiev and Diamond, 2009). The yellow line shows the boundary of the hydrothermal convection zone and the heat conduction zone (Doi *et al*., 1998).

5. Geochemical evolution of the permeable-impermeable boundary

Simulation of dissolution and precipitation of silica minerals along the well WD-1a of the Kakkonda geothermal field was conducted by using the new kinetic equation of overall silica-water interaction derived in the chapter 3. Amount of dissolution and precipitation of silica minerals increases with decreasing of the fracture permeability from 1×10^{-9} to 1×10^{-13} m^2. The largest amount of silica precipitation could occur in the

downflow fluid at 3150 m depth regardless of the permeability. At the shallower part, the time for fracture sealing at the fracture permeability of 1×10^{-13} m^2 correlates with the estimated ages in the previous studies of the Kakkonda geothermal field as ~0.2 Ma, whereas that at the permeable-impermeable boundary is ~1000 years, which is ~100 times faster than the results in the previous works (Fig. 5), indicating that the division of the permeable and impermeable area might occur at the early stage in the evolution of the Kakkonda geothermal field.

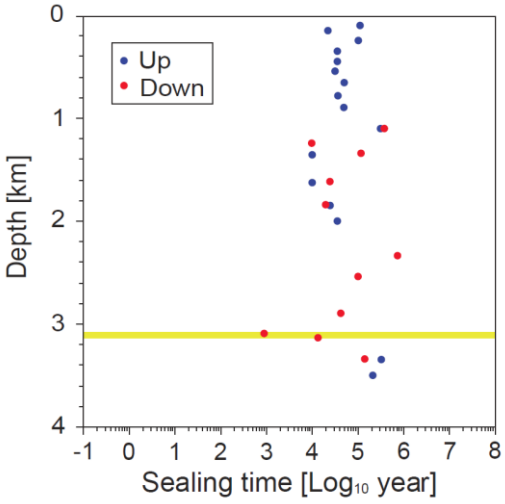

Figure 5 Sealing time of a parallel fracture at fracture permeability of 1×10^{-13} m^2. Silica precipitation occurs in upward- (blue) and downward- (red) fluids. The permeable-impermeable boundary in the well WD-1a of the Kakkonda geothermal field is at 3100 m depth (yellow line).

6. Conclusions

The hydrothermal flow-through experiments revealed that (1) large amount of silica precipitation occurs in the supercritical conditions of water, and (2) mineralogy of silica precipitates changes and precipitation rate increases depends on Al and Na concentrations in the input solution. The kinetic equation of overall silica-water interaction was derived empirically. Calculation of quartz solubility revealed that the depth of a local minimum of quartz solubility correlates with that of the permeable-impermeable boundary at the Kakkonda geothermal field, Japan. The rapid quartz precipitation plays a significant role in forming and sustaining the permeable-impermeable boundary within the Earth's crust, especially at geothermal fields.

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（別紙）

論文審査結果の要旨及びその担当者

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論　文　題　目	Geochemical evolution of the permeable-impermeable boundary within the Earth's crust revealed by silica precipitation （シリカ鉱物析出による地殻の透水－不透水境界の地球化学的発展）
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論文審査結果の要旨

シリカ(SiO_2)は，地殻中に最も多く含まれる成分であり，シリカ鉱物の溶解・析出現象は，地殻の地球化学的性質を決定する重要な要素反応である。しかしながら，地殻流体の超臨界状態でのシリカ鉱物の析出現象についての検討は遅れ，亜臨界条件での現象の高温外挿でしか考察するすべがなかった。超臨界状態を含むような高温地熱地帯においては，地殻内での流体の透水性の境界があることが指摘されていたにもかかわらず，その理由について明快な回答を得ることができておらず，高温地熱貯留層の開発に大きな障壁となっていた。本研究は，超臨界条件下でのシリカ鉱物の析出反応実験を行い，この結果を基に，地殻の透水性の地球化学的発展プロセスを論じたもので，全編5章よりなる。

第1章は，緒論である。

第2章は，超臨界条件でのシリカ鉱物の析出実験についてまとめている。シリカ溶解度は超臨界状態でいったん大きく落ち込むことが知られており，本研究ではこの性質を用いて，亜臨界状態の高溶解度環境で花崗岩を溶解し，超臨界状態では過飽和の溶液を作り出し，これを反応管内に流通させてシリカ鉱物の析出を引き起こした。その結果，シリカ鉱物の析出は表面反応による析出と，核生成による析出の2つの様式に大別され，それぞれの様式が支配的になる条件を明らかにすることができた。また，超臨界条件でのシリカの析出は石英の核生成に起因し，その析出に及ぼす不純物（Al, Na)の影響を定量的に評価することに成功している。これはきわめて大きな成果である。

第3章は，シリカの析出速度式について考察し，表面反応と核生成による析出の2つの項を含む析出速度式を提案している。この式により，超臨界条件を含む広い範囲でのシリカの析出速度を求めることが可能となった。シリカの析出速度式は，1980年に公表されたものが広く用いられてきたが，本研究により，超臨界状態まで拡張した速度式が得られ，当該分野に大きな進歩をもたらした。きわめて大きな成果である。

第4章は，葛根田地熱地帯をモデルフィールドにして，地熱貯留層でのシリカの析出を解析し，地殻の透水性の変化はシリカ鉱物の析出に強く関係していることを見いだしている。この研究により，熱水対流ゾーンと熱伝導ゾーンの境界はシリカ鉱物の析出により区切られている可能性を指摘し，地殻の透水－不透水境界の地球化学的意味を明らかにしている。この成果は，地熱貯留層の発達を考察するうえで重要な成果である。

第5章は，き裂型地熱貯留層でのシリカ鉱物の析出に関する数値シミュレーションを行い，地殻の透水－不透水境界の発達プロセスならびに地熱貯留層の地球化学発展プロセスを提示している。シリカ鉱物の溶解析出現象と貯留層の発展のプロセスを融合させたシミュレーションとして有用であり，地熱貯留層の新たな地球化学的評価方法として大きく展開することが期待できる。

第6章は結論であり，本研究で得られた成果をまとめている。

以上要するに本研究は，超臨界状態を含む熱水環境下でのシリカ鉱物の析出プロセスを実験的に検討し，その析出メカニズムと析出速度式を明らかにし，その成果を基礎として地殻の透水－不透水境界の発達プロセスを解明して，地熱貯留層の地球化学的発達過程を明らかにしたもので，水熱化学，地球化学ならびに環境科学の発展に寄与するところが少なくない。

よって，本論文は博士(学術)の学位論文として合格と認める。